of the series F, Cl, and Br, CHBr is expected to have the smallest ΔE(S–T), assuming the singlet carbene is in each case the ground state. The same results may be understood in terms of the π-donor abilities[50–52] of the substituents F, Cl, and Br.

At the SCF level of theory, triplet CHBr is incorrectly predicted to be the ground state, lying 12.6 kcal below the lowest singlet state. However, when the TCSCF description (3) is used for the singlet state, the latter falls lower in energy, but by only 0.7 kcal. Higher levels of theory further preferentially stabilize singlet CHBr, leading ultimately to a 4.1-kcal value for ΔE(S–T). This result differs by 5.2 kcal from the BSB prediction[9] that triplet CHBr lies 1.1 kcal below the lowest singlet state. Including estimated error bars, our predicted singlet–triplet energy difference is 4.1 ± 2 kcal.

Vibrational frequency and IR intensity predictions for bromocarbene are given in Table VI. Reducing the TCSCF frequencies by 10% for ground-state singlet CHBr yields 2848 cm^{-1} (C–H stretch), 611 cm^{-1} (C–Br stretch), and 1120 cm^{-1} (bending). Since triplet CHBr is predicted to lie only 4.1 kcal higher, it is not inconceivable that its infrared spectrum might be observed in the not-too-distant future. Singlet and triplet CHBr should in principle be distinguishable by the prediction that the triplet C–H stretching frequency lies 176 cm^{-1} higher, at 3023 cm^{-1}. The problem is that the IR intensity of the C–H stretch for all three triplet monohalocarbenes is rather low, less than 0.1 km/mol. For both singlet and triplet states of all three molecules, the carbon–halogen stretching frequency is predicted to be the most intense among the three fundamentals.

Some Concluding Comparisons

The theoretical predictions reported here are for the most part consistent with what is known experimentally about the carbenes CHF, CHCl, and CHBr. Exceptions are the CH distances in singlet CHF and (perhaps) CHCl and the C–H stretching frequency of fluorocarbene. In addition, we provide predictions of many properties of these molecules not yet observed in the laboratory. Most notably there is apparently no spectroscopic observation to date of CHBr. The remainder of this concluding section is devoted to comparisons between the three carbenes.

The dipole moments of the three molecules are predicted in Table VI and that of singlet CH_2 at a comparable level of theory is reported elsewhere.[53] For the lowest singlet states, the predicted TZ+2P TCSCF dipole moments are −1.66 (CH_2), 1.44 (CHF), 1.44 (CHCl), and 1.39 (CHBr) D. The halocarbene dipole moments are essentially equal and show little dependence on halogen atom electronegativity. The predicted triplet-state dipole moments from TZ+2P SCF theory are −0.59 (CH_2), 1.32 (CHF), 1.15 (CHCl), and 1.13 (CHBr).

The only experimental information concerning halocarbene dipole moments comes from the paper by Dixon and Wright.[19] For the $\tilde{X}\ ^1A'$ ground state of CHF, they find $\mu_a = 0.061 \pm 0.005$ D, where μ_a is the dipole moment along the a rotational axis. Dixon and Wright also suggest that the dipole moment component μ_b could also be quite large (≈1 D). For singlet CHF, the present TCSCF theory predicts $\mu_a = 0.36$ and $\mu_b = 1.40$ D.

Errors of this magnitude (0.3 D) for dipole moments are not unusual at the Hartree–Fock level of theory.[54] Therefore, it was decided to evaluate the dipole moment using the configuration interaction (CISD) method. The results, $\mu_a = 0.066$ and $\mu_b = 1.424$ D, are in essentially perfect agreement with the experimental μ_a value of Dixon and Wright.[19]

Acknowledgment. This research was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the US Department of Energy under Contract DE-AC03-76SF00098. The Berkeley theoretical chemistry minicomputer is supported by the US National Science Foundation, Grant CHE-8218785. M.D. wishes to acknowledge the financial support of the Generalitat de Catalunya.

Note Added in Proof. D. G. Leopold and W. C. Lineberger informed us on April 8 that they have experimentally determined an upper limit of 15 kcal/mol for the singlet–triplet energy separation for CHF. This is consistent with the present theoretical prediction of 13.2 kcal/mol.

Registry No. CHF, 13453-52-6; CHCl, 2108-20-5; CHBr, 17141-28-5.

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Mechanism of the Thermal [1,5]-H Shift in *cis*-1,3-Pentadiene. Kinetic Isotope Effect and Vibrationally Assisted Tunneling

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Abstract: Ab initio 3-21G calculations have been performed for the [1,5]-H shift in *cis*-1,3-pentadiene. A transition state of C_s symmetry has been compared with one of C_{2v} symmetry. The lowest energy configuration of this latter structure has B_1 symmetry and must therefore be described by an open-shell calculation. The energy of this structure is favored by 5.2 kcal/mol over the one of C_s symmetry. Both structures are found to be real transition states. Both the calculated reaction rates and the kinetic isotope effects are found to be considerably smaller than the observed ones. A mechanism is suggested in which tunneling takes place between high-vibrational states of the reactant and the product. It is shown that this mechanism is most likely for the transition state of C_{2v} symmetry. The calculated tunneling rates indicate that the [1,5]-H shift in *cis*-1,3-pentadiene mainly takes place via this mechanism.

The thermal [1,5]-H shift in *cis*-1,3-pentadiene is an example of the general class of sigmatropic reactions (Scheme I). In 1966, Roth and König[1] studied this reaction in the temperature range of 185–210 °C. They established an activation enthalpy of 35.4 kcal/mol and a kinetic isotope effect (KIE) for $k_H/k_D = 5.1$. The temperature dependence of the KIE was found to be $k_H/k_D = 1.15 \exp(1.4(\text{kcal/mol})/RT)$. From these observations they concluded that the reaction is a concerted process which proceeds through a symmetric pericyclic transition state (TS), thus confirming the predictions based on orbital symmetry considerations.

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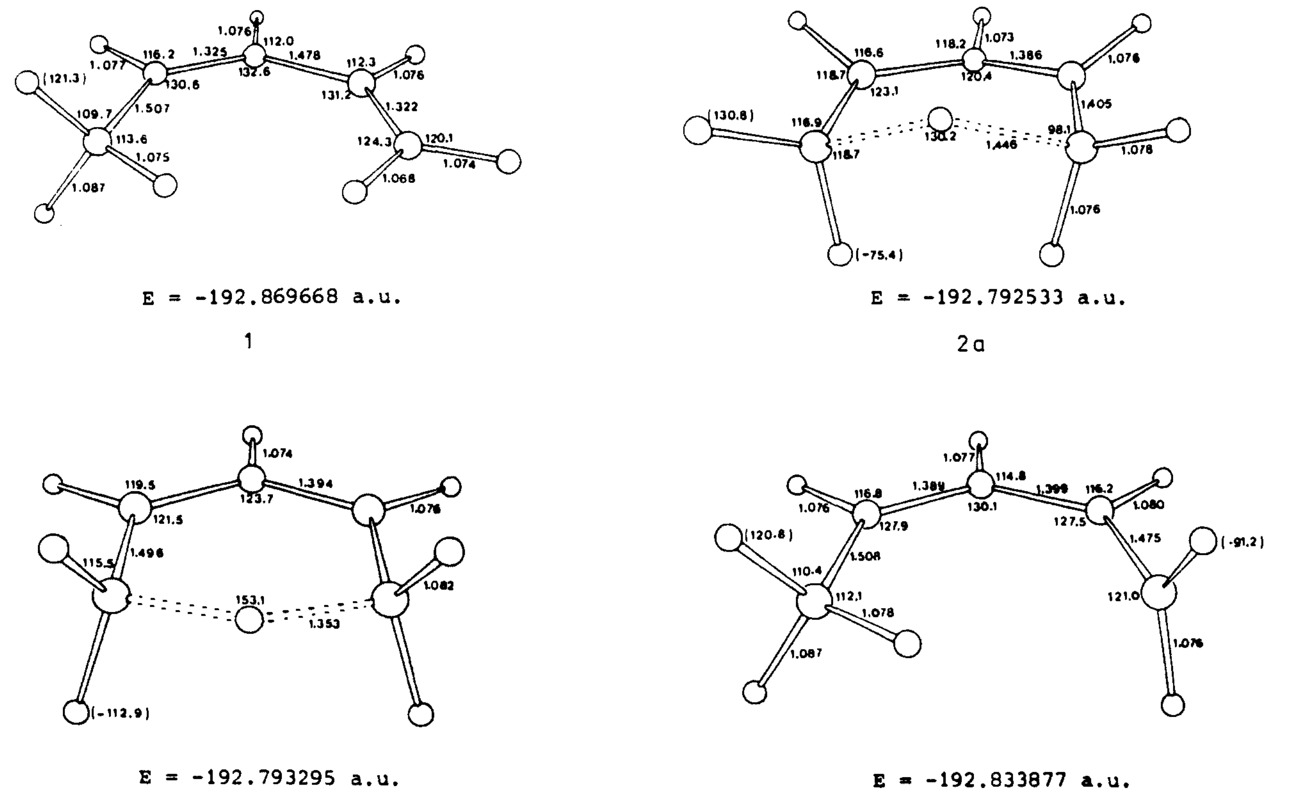
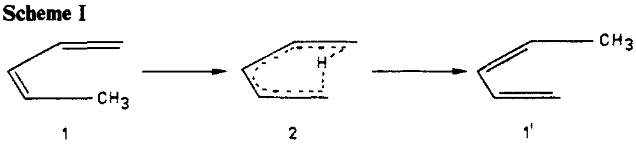


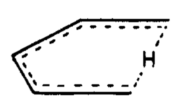
Figure 1. 3-21G-optimized structures and energies for the reactant (**1**), the transition states of C_s symmetry (**2a**) and C_{2v} symmetry (**2b**), and the twisted reactant (**3**).

Scheme I



1 2 1'

Chart I



Kwart[2] used this temperature dependence of the KIE as a criterion for the geometry of the TS involved. In particular, a temperature-independent KIE should be associated with a bent TS. In view of these facts, Kwart et al.[3] concluded that the TS for the [1,5]-H shift in *cis*-1,3-pentadiene must have a collinear arrangement of the migrating hydrogen atom and the two terminal carbon atoms (Chart I). However, the use of the temperature dependence of the KIE as a mechanistic criterion has been questioned recently.[4-6] It was found[6] that both a linear and a bent TS have a temperature-dependent KIE, the latter being somewhat smaller due to a greater sensitivity of the bending vibrations to isotopic substitution. Further indications for a nonlinear TS were given by quantum chemical calculations at the semiempirical[7,8] and ab initio[9-11] levels of computation. In all cases, it was found that the TS has an acute angle at the migrating hydrogen atom. Hess and Schaad[10] noticed that the collinear TS has C_{2v} symmetry. They optimized this structure at the RHF/3-21G level and compared it with a bent TS of C_s symmetry. It was found that the former one is considerably higher in energy (67.7 kcal/mol). Moreover, the optimized C_{2v} TS has a distinct angle of 151.9° at the migrating hydrogen atom. A TS with a collinear arrangement would even be higher in energy. In our study on the mechanism of sigmatropic shifts,[12] we found that the lowest energy configuration (ground state) of the C_{2v} TS has B_1 symmetry and therefore cannot be described by a closed-shell RHF calculation. In contrast, the ground state of the C_s TS does have A′ symmetry. So a comparison of these two TSs is incorrect. All calculated reaction enthalpies[7-12] and KIEs[8,10b] show a large discrepancy with the observed parameters.[1] From these facts, Dewar[8] concluded that quantum chemical tunneling might play an important role in this reaction. However, the geometries of the reactant (**1**) and the product (**1′**) differ too much to make direct tunneling likely (Scheme II). Therefore, he proposed a mechanism (vibrationally assisted tunneling: VAT) in which tunneling takes place from a twisted form of the reactant (**3**) to a twisted form of the product (**3′**) via a TS of C_s symmetry. The only geometrical change involved then is the position of the migrating hydrogen atom. Dewar's MINDO/3 calculations showed that the [1,5]-H shift should proceed dominantly via VAT in the temperature range of 185–210 °C. In this paper both TSs of C_{2v} and C_s symmetry are compared by an appropriate SCF-geometry optimization with the 3-21G basis set. A complete vibrational analysis is presented from which the KIE and VAT tunneling rates are calculated. The difference between the two TSs is best accentuated for the tunneling mechanism, which is most likely to proceed via the TS of C_{2v} symmetry.

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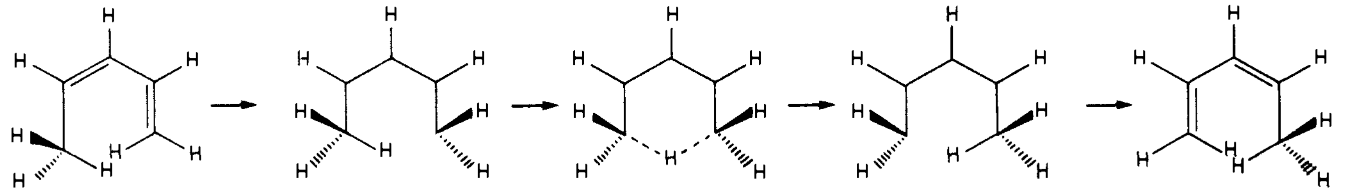
Scheme II



1 3 2 3' 1'

Table I. Calculated (3-21G) Harmonic Vibrational Frequencies for Structures **1**–**3**[a–c]

	1		2a		2b		3
a′	3317 (3315)	a′	3247 (3247)	a_1	3242 (3242)	a′	3310* (2420*)
	3247 (2369)		3320 (3219)		3216 (3213)		3230 (3230)
	3234 (3234)		3176 (3176)		3160 (3160)		3218 (3219)
	3225 (3225)		1715 (1690)		1731 (1189)		3201 (3201)
	3218 (3217)		1632 (1209)		1527 (1462)		3170 (3170)
	3214 (3214)		1625 (1608)		1457 (1455)		3119 (3119)
	3120 (3114)		1584 (1555)		1380 (1369)		1673 (1317)
	1876 (1876)		1540 (1492)		950 (931)		1488 (1475)
	1785 (1785)		1468 (1383)		780 (776)		1425 (1425)
	1674 (1625)		1338 (1328)		671 (666)		1395 (1395)
	1670 (1477)		1218 (1215)		224 (219)		1331 (1331)
	1494 (1494)		1124 (1052)	a_2	3268 (3268)		1273 (1269)
	1419 (1411)		1053 (1025)		1067 (1048)		1262 (1252)
	1332 (1323)		852 (816)		974 (969)		1181 (1175)
	1280 (1277)		726 (699)		279 (278)		1069 (1047)
	1271 (1258)		610 (601)		229 (229)		973 (973)
	1249 (1212)		529 (522)	b_1	3248 (3247)		863 (861)
	1211 (1190)		452 (447)		1575 (1561)		758 (718)
	1162 (1006)	a″	3274 (3274)		1293 (1261)		462 (458)
	764 (723)		3261 (3261)		956 (951)		340 (327)
	354 (340)		3226 (3226)		832 (830)		263 (242)
	168 (158)		3172 (3172)		587 (573)	a″	3300 (3300)
a″	3206 (3206)		1679 (1661)		434 (409)		3197 (3197)
	1217 (1212)		1606 (1589)	b_2	3225 (3225)		1786 (1785)
	1172 (1141)		1526 (1471)		3149 (3149)		1677 (1620)
	1135 (1127)		1489 (1461)		2022 (1834)		1638 (1638)
	1059 (1059)		1360 (1351)		1566 (1537)		1454 (1442)
	919 (919)		1277 (1277)		1358 (1345)		1307 (1306)
	880 (878)		1232 (1226)		1346 (1340)		1254 (1248)
	650 (635)		1139 (1136)		1257 (1231)		1080 (992)
	374 (364)		1009 (995)		1194 (1194)		393 (387)
	323 (308)		311 (311)		1122 (1096)		238 (232)
	144 (143)		1925i (1521i)		2206i (1830i)		565i (565i)

[a] Units are in cm^{-1}. [b] The frequencies of the structures where the migrating hydrogen atom is substituted by a deuterium are given in parentheses. [c] The reaction coordinate mode for the twisted structure **3** is marked with an asterisk.

Calculational Method and Results

Calculations were performed with the GAUSSIAN 80 program system.[13] The relevant structures **1**, **2a**, **2b**, and **3** were fully optimized with the 3-21G basis set,[14] using the RHF Hamiltonian for the closed-shell structures **1** and **2a** and the UHF Hamiltonian for the open-shell structures **2b** (B_1 symmetry) and **3** (A″ symmetry). The resulting geometries and energies are given in Figure 1. Hess and Schaad[10b] found that the geometries for similar sigmatropic shifts are almost unaffected by the size of the basis set used. So we have not reoptimized the 3-21G structures with a larger basis set. The bare potential energy barriers for the reactions via **2a** and **2b** are 48.4 and 47.9 kcal/mol, respectively. This difference might be affected by larger basis sets and calculations at a higher level of theory (configuration interaction and perturbation treatment[12]). However, as we have performed the vibrational analysis for the 3-21G geometries, it is consistent to use the corresponding energies in the rest of the calculations. It is seen that both structures **2a** and **2b** show a distinct angle at the migrating hydrogen atom. These CHC angles are 130.2° (**2a**) and 153.1° (**2b**), respectively. This confirms earlier suggestions that the TS for the [1,5]-H shift in *cis*-1,3-pentadiene does not have a collinear arrangement as supposed by Kwart et al.[3] For each structure we calculated the force constant matrix by finite differences (0.005 au) from analytical first derivatives of the energy. Vibrational frequencies and corresponding normal modes were calculated by using the conventional FG method.[15] The vibrational frequencies of the deuterated molecules were calculated using the same force constant matrix. The results are given in Table I. It is seen that the structures **2a**, **2b**, and **3** are characterized by a single imaginary frequency, which means that these three structures represent a real TS. For **2a** and **2b**, the corresponding normal modes show a horizontal movement of the migrating hydrogen atom toward one of the terminal carbon atoms, thus representing a real hydrogen shift. For structure **3**, the imaginary frequency corresponds to the thermal twist of the terminal double bond. This structure therefore is a TS for the *E*–*Z* isomerization of this bond.[16] A comparison of the vibrational frequencies of **1** with the experimental ones of 1,3-pentadiene[17] shows that the 3-21G frequencies are systematically overestimated by ca. 10%, which is in agreement with similar calculations.[18]

Classical Reaction Rates and Kinetic Isotope Effect

In Table II we give the activation parameters for the [1,5]-shift via the structures **2a** and **2b**. These parameters have been cal-

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Table II. Calculated (3-21G) and Experimental Activation Parameters and Reaction Rates for the [1,5]-Shift in *cis*-1,3-Pentadiene at 473 K

	reaction via					
	2a		2b		obsd[a]	
	H	D	H	D	H	D
$\Delta H^{\ddagger\,b}$	48.8	49.6	43.6	44.2	35.4	36.8
$\Delta S^{\ddagger\,c}$	-8.3	-8.6	-3.8	-4.0	-7.1	-7.4
k^d	1.1×10^{-11}	4.3×10^{-12}	3.0×10^{-8}	1.3×10^{-8}	4.5×10^{-6}	0.9×10^{-6}

[a] Reference 1. [b] Activation enthalpies ($\Delta H^{\ddagger}$) in kcal/mol corrected for zero-point energies relative to **1**. The bare potential energy barriers are 48.4 (**2a**) and 47.9 (**2b**) kcal/mol. [c] Activation entropies ($\Delta S^{\ddagger}$) in cal/(mol K). [d] Reaction rates in s^{-1} calculated from the parameters in this table.

Table III. Calculated (3-21G) and Observed Kinetic Isotope Effects (k_H/k_D) for the [1,5]-Shift as a Function of Temperature. Results Have Been Obtained from Equation 1 (See Text)

	reaction via		
T,[a] K	2a	2b	obsd[b]
460	2.52	2.18	5.32
470	2.48	2.15	5.15
480	2.44	2.12	4.99
490	2.40	2.09	4.84

[a] Absolute temperatures. [b] Results for the observed KIE: $k_H/k_D = 1.15 \exp(1.4(\text{kcal/mol})/RT)$; see ref 1.

culated from the frequencies in Table I by using the rigid-rotor–harmonic oscillator approximation. The activation enthalpies corrected for zero-point energies for the [1,5]-H shift via **2a** and **2b** are 48.8 and 43.6 kcal/mol. The enthalpy difference of 5.2 kcal/mol comes mainly (4.7 kcal/mol) from the differences in the zero-point energies for the two TSs. The reason for this is the shift of the skeletal vibrations of the bent TS **2a** toward higher wavenumbers (see Table I). This effect is also reflected in a more negative entropy of activation for this reaction. From the activation parameters we calculated the classical reaction rates (neglecting tunneling) from transition-state theory. These rates are also given in Table II. It is seen that the calculated rates are considerably smaller than the observed ones, which is hardly astonishing in view of the calculated activation enthalpies. Within the transition-state theory, it is also possible to calculate the KIE. According to this theory, the KIE arises from differential changes in the entropies and enthalpies of the reactant and the TS due to isotopic substitution. It depends on both the geometries (moments of inertia) and the vibrational frequencies of the TS involved. Therefore, it is expected that the KIE should give detailed information about the structure of the TS. We calculated the KIE from Bigeleisen's equation[19] (1) (which is a rigid-rotor–harmonic oscillator approximation). In this equation, $\nu_H^{\ddagger}/\nu_D^{\ddagger}$

$$k_H/k_D = \nu_H^{\ddagger}/\nu_D^{\ddagger}\cdot \text{EXC}\cdot\text{ZPE}\cdot\text{VP} \qquad (1)$$

is the isotopic ratio of the imaginary frequencies representing motion along the reaction coordinate in the TS. In Bigeleisen's formulation it represents the KIE at an infinite temperature and it equals the result obtained from classical theory. All other terms are pure quantum mechanically in origin. The VP is a vibrational frequency product, EXC a vibrational excitation term, and ZPE the contribution due to differences in the vibrational zero-point energies. The equation originates from the assumption that isotopic substitution does not influence the geometries and potential energy surfaces. The results for the KIE as a function of temperature are given in Figure 2 and Table III. From these values, we calculated the temperature dependence of the KIE for the reactions via **2a** and **2b** (see Table IV). Both reactions show a temperature-dependent KIE, in contrast to Kwart's suggestion[2] that a bent TS should be associated with a temperature-independent KIE. The calculated ΔE_D^H values are considerably smaller than the observed one.[1] This is reflected in the value for the KIE at room temperature. For the reactions via **2a** and **2b**, k_H/k_D equals 3.9 and 3.2, respectively. The extrapolated value

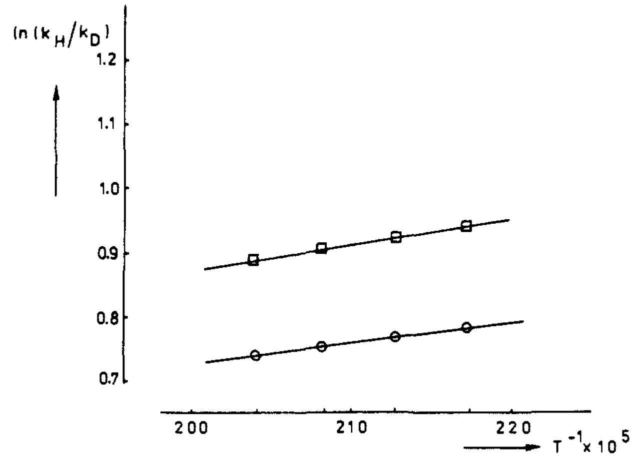

Figure 2. Temperature dependence of k_H/k_D for the thermal [1,5]-H shift in *cis*-1,3-pentadiene. (□) Reaction via transition state **2a**. (○) Reaction via transition state **2b**.

Table IV. Temperature Dependence of the Kinetic Isotope Effect

	reaction via		
	2a	2b	obsd[a]
$\Delta E_D^{H\,b}$	0.73	0.63	1.40
$A_H/A_D{}^c$	1.14	1.09	1.15
k_H/k_D (473 K)	2.5	2.1	5.1
k_H/k_D (298 K)	3.9	3.2	12.2

[a] See ref 1. [b] Activation energy difference for H and D transfer in kcal/mol. [c] Preexponential frequency factor ratio.

for the experimental KIE at this temperature is 12.2, which is anomalously large. On the other hand, the calculated frequency factor ratio A_H/A_D is of comparable size and in line with other theoretical predictions.[6,20] When the KIEs for the two reactions are compared, it is seen that the TS with the larger angle at the migrating hydrogen atom (**2b**, 153.1°) shows the smaller KIE. The same relation holds for the temperature dependence (ΔE_D^H) of the KIE. Thus, where it is frequently assumed that a larger angle should be associated with a larger temperature dependence of the KIE,[21] our calculations show that this criterion should not be used. Both the calculated reaction rates and the KIEs are considerably smaller than the observed ones. This may be caused by deficiencies in the calculational method. It is clear that the reaction rates are sensitive to the activation parameters, which depend on the calculated bare potential barriers and the harmonic vibration frequencies. However, it is not expected that the differences between calculated and observed activation energies will be completely cancelled by using larger basis sets[10b] or configuration interaction and perturbation treatments.[12] The calculated vibrational frequencies deviate by 10% from the observed ones (vide supra), and corresponding errors in the enthalpies and entropies are therefore expected to be relatively small. The calculations have been performed within transition-state theory which implies the simplifying feature that the geometries and force

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(21) When our calculated values for (the temperature dependence of) the KIE are fitted to the values from the model study of McLennan and Gill,[6] we must use their model B for our TS **2a** and their model C for our TS **2b**.

constant matrices are independent of isotopic substitution. However, especially for a reaction where a light atom is transferred between two heavy atom fragments via a symmetric or nearly symmetric TS, this approximation breaks down.[22] In such a case, the TSs should be variationally optimized separately for the hydrogen and the deuterium-substituted structures,[23] which generally leads to lower reaction rates. This effect is larger for the reaction in which a hydrogen atom is transferred than for a deuterium exchange.[24] In our case, such an optimization would therefore lead to even lower reaction rates and smaller KIEs.

Vibrationally Assisted Tunneling

A complete description of the tunneling mechanism for the [1,5]-H shift in *cis*-1,3-pentadiene would involve the calculation of the tunneling rate going directly from the reactant (**1**) to the product (**1′**). Such an approach requires the detailed knowledge of the $(3N - 6)$-dimensional potential energy surface, which is out of the question. An approximate solution to this practical problem would be the use of the reaction path Hamiltonian.[25] The only data needed then, are the potential energy and all force constants along a reaction path, which is choosen as the steepest descent path in mass-weighted coordinates through the TS. However, even this one-dimensional approach runs into difficulties in regions where the reaction path has a large curvature. It was pointed out by Carrington and Miller[22b] that a more accurate description of such a situation requires at least 2 reaction-like degrees of freedom. However, a calculation based on this reaction surface Hamiltonian is still a very time-consuming matter for a molecular system of the dimensions of pentadiene. In the VAT model of Dewar,[8] tunneling takes place from a twisted form of the reactant (**3**) to a twisted form of the product (**3′**). The geometrical changes involved are then restricted to the motion of the migrating atom between the two terminal carbon atoms. We have elaborated this suggestion through a geometry optimization of the twisted structure (see Figure 1). The energy needed to distort the reactant to the twisted form is 22.41 kcal/mol (corrected for zero-point energies). In our earlier work,[12] we showed that this structure directly correlates with the TS of C_{2v} symmetry, which makes this TS to be especially suited for VAT. Tunneling via the C_s TS asks for more drastic geometrical changes. We have calculated the tunneling rates going from the twisted reactant (**3**) to the twisted product (**3′**) via the TSs of C_s and C_{2v} symmetry following the procedure described by Bicerano et al.[26] They obtained encouraging results with a one-dimensional approximation of the tunneling dynamics for proton transfer in malonaldehyde. Our model for tunneling between the two twisted structures in *cis*-1,3-pentadiene is very similar to this model system. The calculation is based on the method of periodic orbits for one-dimensional tunneling in a symmetric double well potential.[27] In this model, the tunneling rate ω_n is given by eq 2 in which ΔE_n

$$\omega_n = 2\Delta E_n/h \tag{2}$$

is the splitting of the energy levels in the two potential wells due to tunneling. For small splittings, ΔE_n can be calculated within the WKB approximation by[28] eq 3.

$$\Delta E_n = \frac{h\nu_F}{\pi}e^{-\theta_n} \tag{3}$$

Here, ν_F is the (harmonic) vibration frequency of the normal mode F which leads to reaction. It is obvious to choose for this mode the C–H-stretching vibration of the hydrogen atom that tunnels (see Table I). When the potential barrier is approximated by an Eckart function,[29] the penetration integral θ_n is given by eq 4. In this expression, ν_i is the imaginary frequency which

$$\theta_n = \frac{2\pi}{\hbar\nu_i}[V_{\text{eff}} - (E_nV_{\text{eff}})^{1/2}] \tag{4}$$

corresponds to the reaction coordinate motion in the TS. V_{eff} is the effective energy difference between the lowest vibrational state in one of the potential wells and the first vibrational level at the top of the potential barrier.[26] In the harmonic approximation, E_n is given by eq 5. In the VAT model, it is necessary to include tunneling from all bound vibrational states of the normal mode F. The overall tunneling rate is then eq 6.

$$E_n = \tfrac{1}{2}(n + 1)\hbar\nu_F \qquad n = 0, 1, 2, \text{etc.} \tag{5}$$

$$k_t = e^{-\Delta E_a/RT}\sum_{n=0}^{N-1} f_n\omega_n \tag{6}$$

In this equation, ΔE_a is the energy needed to distort the reactant (**1**) to the twisted structure (**3**), f_n the fraction of the molecules in the vibrational state with energy E_n, and ω_n the tunneling rate as calculated from eq 2–5. The summation is carried out for all N states below the barrier maximum. For both reactions via **2a** and **2b**, there are three bound vibrational states for the hydrogen shift and four bound vibrational states for the deuterium shift. We used the vibrational frequencies from Table I. As indicated earlier, these values are overestimated by ca. 10% so that we have scaled down all frequencies (including the imaginary) in the calculation by this factor. In Table V, the results are given for the calculation of the overall tunneling rate k_t for the two reactions via **2a** and **2b** in the temperature range in which the [1,5]-H shift in *cis*-1,3-pentadiene has been studied. From a comparison of Tables I and V, it is seen that the calculated tunneling rates are larger than the calculated classical reaction rates by several powers of 10. This indicates that the proposed mechanism of VAT should indeed play an important role for this sigmatropic shift. Tunneling is found to be more efficient for the reaction via the TS of C_{2v} symmetry than for the reaction via the TS of C_s symmetry. The reason for this is partly the lower activation energy for the former reaction, but more decisive is the larger imaginary frequency for the reaction coordinate mode of this TS which is a measure for the width of the barrier between the two potential wells.[30] The VAT model introduces a strong temperature dependence of the tunneling rates (see Table V) which is markedly different for hydrogen and deuterium transfer. For example, an Arrhenius plot of the tunneling rates for the reaction via **2b** yields an activation energy of 25.8 kcal/mol for the H shift and 30.7 kcal/mol for the D shift. This difference comes from the fact that for the deuterium shift, the tunneling from higher vibrational states is more important. At this point, it is worth making some reservations about the reliability of these results. It can first be seen that the calculated tunneling rates are relatively sensitive to the

Table V. Calculated (3-21G) VAT Rates (k_t) for the [1,5]-Shift in *cis*-1,3-Pentadiene[a]

	reaction via			
	2a		**2b**	
T,[b] K	H	D	H	D
460	1.7×10^{-7}	2.6×10^{-9}	7.8×10^{-5}	3.0×10^{-6}
470	3.4×10^{-7}	6.0×10^{-9}	1.4×10^{-4}	6.1×10^{-6}
480	5.9×10^{-7}	1.4×10^{-8}	2.5×10^{-4}	1.2×10^{-5}
490	1.3×10^{-6}	3.0×10^{-8}	4.4×10^{-4}	2.3×10^{-5}

[a] Tunneling rates (in s^{-1}) have been calculated from eq 2–6 using the frequencies given in Table I (scaled down by 10%; see text). [b] Absolute temperatures.

(22) (a) Such a reaction is characterized by a small skew angle between the reaction paths at the reactant and product sites of the potential energy surface in mass-weighted coordinates. See e.g.: Babamov, V. K.; Marcus, R. A. *J. Chem. Phys.* **1981**, *74*, 1790. Garrett, B. C.; Truhlar, D. G.; Wagner, A. F.; Dunning, T. H. *J. Chem. Phys.* **1983**, *78*, 4400. (b) Carrington, T., Jr.; Miller, W. H. *J. Chem. Phys.* **1984**, *81*, 3942.

(23) See for instance: Truhlar, D. G.; Garrett, B. C. *Ann. Rev. Phys. Chem.* **1984**, *35*, 159.

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(28) See for instance: Harmony, M. D. *Chem. Soc. Rev.* **1972**, *1*, 211.

(29) Bell, R. P. *The Tunnel Effect in Chemistry*; Chapman and Hall: London, 1980.

(30) Notice also that the C–H distance for the migrating hydrogen atom is considerably smaller for the TS of C_{2v} symmetry (1.353 Å) than for the TS of C_s symmetry (1.446 Å).

calculated barrier heights for the twist of the double bond (see eq 6) and the barrier heights for the actual shift (eq 4). The same proviso, however, has to be made for the classical reaction rates. Additionally it was assumed that the vibrational mode F behaves harmonically. For the lowest bound state, this approximation is fairly reasonable, but for the higher bound states, deviations will become more important. Generally, the anharmonicity will lead to a lower tunneling rate ω_n. This will be partly cancelled by an increasing population f_n of the upper vibrational levels so that the overall effect upon the VAT rate k_t is indistinct. As we have obtained the classical reaction rates and the KIE within the harmonic oscillator approximation, it is merely a matter of self-consistency to use this approximation also to calculate the tunneling rates. A further remark must be made about the validity of the one-dimensional approach. In the derivation of the equations, it was assumed that all vibrations (except ν_F) attribute adiabatically to the tunneling rate. As discussed earlier, this approximation becomes less reliable for a large reaction path curvature.[22a] It is to be expected that a more realistic multidimensional model will lead to lower tunneling rates.[31] In view of these facts, it is clear that we must interpret the absolute values with care. However, it was only our intention to calculate within a consistent model whether the tunneling mechanism might play a role in the [1,5]-shift in *cis*-1,3-pentadiene and, if so, via which TS the reaction is most likely to proceed.

(31) See for instance: Bopp, P.; McLaughlin, D. R.; Wolfsberg, M. *Z. Naturforsch., A.* **1982**, *37A*, 398.

Conclusions

The 3-21G calculations strongly support Dewar's suggestion[8] that tunneling from a twisted form of the reactant should play an important role in the mechanism of the thermal [1,5]-H shift in *cis*-1,3-pentadiene. The reaction is found most likely to proceed via the TS of C_{2v} symmetry. Both optimized TSs have an acute angle at the migrating hydrogen atom, which contradicts the suggestion of Kwart et al.[3] that the TS should have a collinear geometry. The calculated KIEs are found to be temperature dependent, thus confirming recent model studies where it was found that not only a linear but also a bent TS should exhibit a temperature-dependent KIE. The mechanism of VAT also shows a temperature dependence which arises from an essentially different origin than the one for the classical reaction kinetics. Arrhenius extrapolation of the results of Roth and König to room temperature and conclusions based thereupon are therefore not justified.

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Ab Initio Heats of Formation of Medium-Sized Hydrocarbons. 5. A $(CH)_{12}$ Structure Related to the Truncated Tetrahedron[1]

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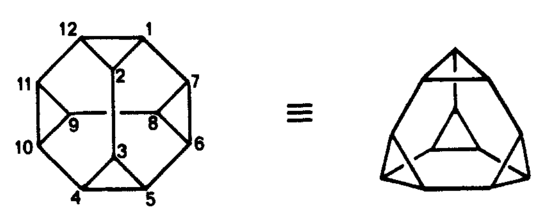
Abstract: The geometry and energy of the $C_{12}H_{12}$ hydrocarbon I, whose carbon framework closely approximates a truncated tetrahedron, was studied by ab initio SCF calculation. Two possible precursors of I are also examined: the triene II, which is more stable than I by ca. 16 kcal/mol, and the tetraene III, which is less stable than I by ca. 24 kcal/mol. The standard heat of formation of I is found to be ca. 91 kcal/mol.

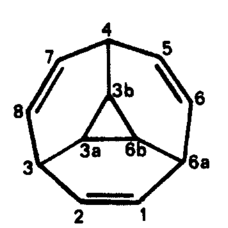
I. Introduction

A curious and as yet unknown $C_{12}H_{12}$ hydrocarbon is the dodecane I, whose carbon framework consists of four planar cyclohexanes and four cyclopropanes. It is formally derived from tetrahedrane by successive replacement of CH apical units with C_3H_3 moieties (truncation[2]), leading via prismane,[3] cuneane,[4] and diademane[5] (all known) to the fourfold trishomobenzene I.[6]

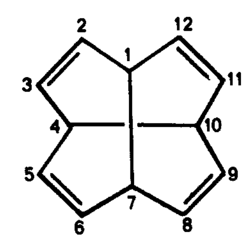
Woodward and Hoffmann[7] pointed out that the tetraene III is a potential photochemical precursor of I by a totally antarafacial $[2_a + 2_a + 2_a + 2_a]$ cycloaddition; no attempt to prepare III has yet succeeded.[8] Similarly, the triene II, a potential precursor



I



II



III

(1) For part 4 of this series see: Schulman, J. M.; Disch, R. L. *Tetrahedron Lett.* **1985**, *26*, 5647.

(2) The process of truncation can of course be applied to other cyclic and acyclic hydrocarbons containing methine groups. Truncation applied to tetrahedrane, cubane, and dodecahedrane produces C_{12}, C_{24}, and C_{60} frameworks in the form of semiregular convex polyhedra whose faces are regular polygons, namely, the truncated tetrahedron, truncated cube, and truncated dodecahedron. See, for example; Lyusternik, L. A. *Convex Figures and Polyhedra*; Dover Publications: New York, 1963.

(3) Katz, T. J.; Acton, N. *J. Am. Chem. Soc.* **1973**, *95*, 2738.

(4) Cassar, L.; Eaton, P. E.; Halpern, J. *J. Am. Chem. Soc.* **1970**, *92*, 6366.

(5) de Meijere, A.; Kaufmann, D.; Schallner, O. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 417.

(6) I = heptacyclo[$5.5.0.0^{2,12}.0^{3,5}.0^{4,10}.0^{6,8}.0^{9,11}$]dodecane. II = 3,3a,3b,4,6a,6b-hexahydro-3,4-ethenocyclopropa[*d,e*]naphthalene. III = tricyclo[$5.5.0.0^{4,10}$]dodeca-2,5,8,11-tetraene. The 357 valence isomers of formula $(CH)_{12}$ have been tabulated, see the following: Banciu, M.; Popa, C.; Balaban, A. T. *Chem. Scr.* **1984**, *24*, 28.

(7) Woodward, R. B.; Hoffmann, R. *The Conservation of Orbital Symmetry*; Verlag Chemie: Weinheim, Bergstr., Germany, 1970.

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